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Electrochemistry at Very High Potentials: Oxidation of the Rare Gases and Other Gases in Non-Aqueous Solvents at Ultramicroelectrodes

By

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ELECTROCHEMISTRY AT VERY HIGH POTENTIALS:

OXIDATION OF THE RARE GASES AND OTHER GASES IN NON-AQUEOUS SOLVENTS AT ULTRAMICROELECTRODES.

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ABSTRACT

Ultramicroelectrodes may be used a solvents containing little or no purposely added supporting electrolyte. Under these conditions, the accessible potential range is considerably extended. Oxidation of species with very high ionization potentials can be studied; oxidation of some of the rare gases and oxygen is reported in this work.

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INTRODUCTION

The accessible potential region in a conventional electrochemical experiment is limited by the oxidation or reduction of the solvent or supporting electrolyte. Under ideal conditions, at room temperature, this window can range from something over +3V vs. Ag/Ag^+ (e.g. acetonitrile, SO_2 solvents), to slightly greater than -3V vs. Ag/Ag (e.g. acetonitrile, ammonia, tetrahydrofuran solvents). It is thus impossible to study the redox reactions of species with very low electron affinities or high ionization potentials by ordinary electrochemical methods. It has been demonstrated recently, however, that by reducing the electrode dimensions to very small values, the quantity of supporting electrolyte necessary to develop the electrical double layer can be reduced to low levels (1). It has thus been possible to study electrode reactions in highly resistive media; these include the oxidation of ferrocene in acetonitrile without purposely added supporting electrolyte, oxidation of chromium hexacarbonyl in pure dichloromethane, oxidation of aromatic hydrocarbons in pure benzene, oxidation ferrocene in pure acetone down to -95°C (2). and oxidations in low temperature solid-solution eutectic mixtures and glasses of acetonitrile (3), to mention a few. Elimination of the ionic supporting electrolyte can extend the accessible potential range in those cases where it is the limiting redox reaction. One such example is oxidation in acetonitrile. The oxidation of the anion of all tested supporting electrolytes in this solvent will occur at potentials less than about 3V vs. Ag/Ag*. We have recently demonstrated (4) that voltammetric data can be obtained at much higher oxidation potentials (c.a. 6V vs. Ag/Ag⁺). In this high energy region, it was possible to observe steady state voltammetric behavior for compounds with vertical ionization

potentials as high as 12.70 in These 1 suded n-heptane, cyclopropane, n-pentane, n-butane, and methane. At these high accessible potentials, we have found that it is possible to observe the oxidation of rare gas substrates. Homogeneous electron transfer reactions involving the rare gases and oxygen were first reported by Bartlett et al (5); they have not been investigated by electrochemical methods.

EXPERIMENTAL

Ring ultramicroelectrodes (Figure 1) are conveniently prepared by (a) coating the inner surface of fine capillaries with metal by vapor deposition or reduction of metal screen printing inks applied to those surfaces, followed by controlled collapsing of the capillary around a glass fiber; or conversely. (b) using the same procedures to deposit the metal on a fine glass or quartz fiber. and collapsing a glass tube around it; or mounting the fiber in a glass tube with epoxy resin. The gold ring electrode used in this work was 20µm in diameter and had an average thickness of 7500Å. The platinum microdisk electrode was constructed by sealing a $0.6\mu m$ diameter wire in a glass tube, and then cutting perpendicular to the axis of the tube to expose the disk. The auxiliary pseudoreference electrode was a silver/silver ion assembly mounted in a glass tube which contained a solvent wetted stopcock and a Luggin capillary arrangement. The tip of the Luggin was placed about 1 mm from the tip of the ultramicroelectrode. The cell was a small flask designed to hold 5mL of solution. The electrodes were mounted through ground glass joints to their working positions. The cell was cleaned in hot acid solution (sulfuric nitric: 1/1 V/V), rinsed in triply distilled water, and vacuum dried at 110°C .

The acetonitrile solvent was used as received (Burdick and Jackson, Distilled in Glass, 0.005% nominal water content). Oxygen, methane, and nitrogen were obtained from Matheson (research grade) and were used as received. The other gases used were from Ideal Gas Products (research grade), and were also used as received. These included xenon, carbon monoxide, krypton, and argon.

The cell assembly was mounted on steel clamps inside a 2 ft³ 3/8" thick aluminum Faraday cage. Connection through the cage was made with triaxial bulkhead connectors. All cables used were triaxial, and were rigidly mounted to prevent noise current generation by mechanical friction between the insulator and conductors in the cable.

The electrode potential difference was maintained by waveform generator (Hi Tek Instruments PPR1) added to a battery. Currents were measured on a Keithley 619 picoammeter, and the polarization curves were plotted manually or on a Hewlett Packard 7015 x-y recorder.

RESULTS AND DISCUSSION

Polarization curves for compounds with very high ionization potentials were obtained by the methods described. A polarization for one example, krypton, is shown in Figure 2. In all cases studied, the height of the limiting current plateau is dependent on the partial pressure of the electroactive gas (see also Table I). Currents observed then are not due to discharge ionization or corona discharge into the dielectric solvent system used in the experiments. This clearly indicates that conventional electrochemical reactions may be carried out at very high potentials in dielectric solvent media and that the current is due solely to the electron transfer reaction. In addition, the $E_{1/2}$ values are

dependent on the <u>type</u> of is present. Previous work (3) showed that at very high potentials, a surface polymeric film is formed on the electrode which passivates the electrode; the bulk electrolysis of the solvent is therefore prevented. This insulating film is, however, permeable to small molecules including the those investigated in this work.

Figure 3 is a plot of $E_{1/2}$ vs. I_p for a number of simple compounds which have high vertical ionization potentials. The seven compounds on the right side of the Figure were analyzed in this work, while the hydrocarbon data on the left side represents previous work (6 — It is noticed that for these molecules with very high ionization potentials, the effect of increases in I_p on $E_{1/2}$ is much smaller than for the compounds with smaller ionization potentials.

In the absence of secondary effects, such as large differences in the solvation energies of an oxidized and reduced form of a redox couple, a linear relation between the oxidation potential and the vertical ionization potential of an electroactive species is to be expected. For a simple redox process

we have

$$E_{rev}^{\theta} = -\frac{1}{nF} \left(\Delta G_{R}^{\theta}(SOLVATION) - \Delta G_{O}^{\theta}(SOLVATION) \right) + \frac{I_{p}}{nF} - E_{ref}^{\theta}$$

where the term in brackets represents the change in free energy of solvation between the reduced and oxidized forms of the couple, n is the number of electrons exchanged per mole of reactant. F is the Faraday constant, I_p is the ionization potential, and E^θ_{ref} is the standard potential of the reference electrode, which we will assume to be a constant value here. The same type of

relation will exist in non-standard states if the activities of the species are taken into account:

$$E_{rev} = E_{rev}^{\theta} - \frac{RT}{nF} \ln \frac{a_0^{\sigma}}{a_R^{\sigma}}$$

where a^{σ}_{0} and a^{σ}_{R} are the activities of the oxidized and reduced forms at the electrode surface, respectively. If the difference between the solvation energies of the reduced and oxidized forms is large, then $\rm E_{1/2}$ will be smaller than when the standard free energies of the two species are equal. One fact is immediately evident from Figure 3; the linear relation is obeyed quite well for the larger electroactive species: those which are on the order of, or larger than, the solvent molecule. Solvation of the larger species can only occur after there is solvent structure rearrangement or breaking: an endothermic process which ultimately reduces the total effect of the magnitude of the difference in the standard free energy of solvation of the two species. Smaller ions, however. show a considerable departure from linear behavior of $E_{1/2}$ and I_p with slope unity: very small ions, having therefore a high charge density, are as expected more efficiently solvated into the solvent cage structure. The difference in the solvation energies of the neutral and oxidized species is large, reflecting the large change in size of the two species, and the half wave potential is greatly decreased.

Chemical reaction of the electrogenerated ion is most likely fast in the bulk solution, and in the case of the rare gases results in a regeneration of the starting material, at least to an appreciable extent. At a normal macroelectrode, this reaction would give rise to a catalytic current that is

higher than the expected uncomplicated diffusion limited current. At an ultramicroelectrode, mass transport is very high so that it is likely that most of the regeneration of starting material will take place at distances suitably distant from the working electrode so that the catalytic current will be minimized. This point was demonstrated by comparing the measured limiting current for a solution saturated with krypton with the value calculated from the relations derived previously (4) for the ring ultramicroelectrode. The values were found to be the same within estimated experimental error.

CONCLUSIONS

It is clear that a variety of new and interesting chemical systems may be investigated by taking advantage of the unusual properties of ultramicroelectrodes. High rates of mass transport, reduction of ohmic losses in solution, and low capacitive currents allow measurements to be made under conditions that heretofore have been considered futile. Highly energetic species exhibiting large size changes upon electron transfer may be studied electrochemically due to the great difference in solvation energies of the conjugate redox pair.

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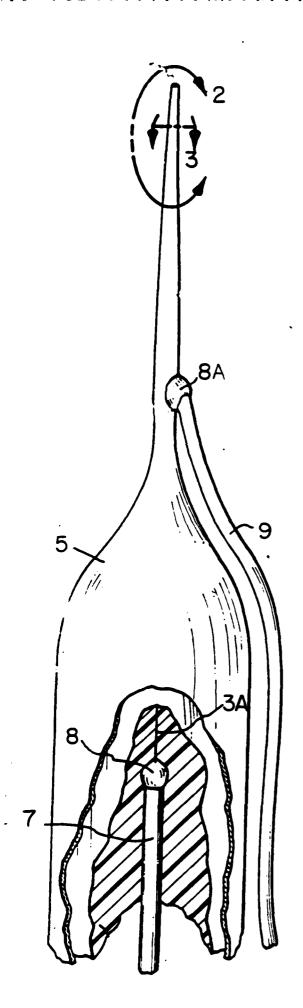
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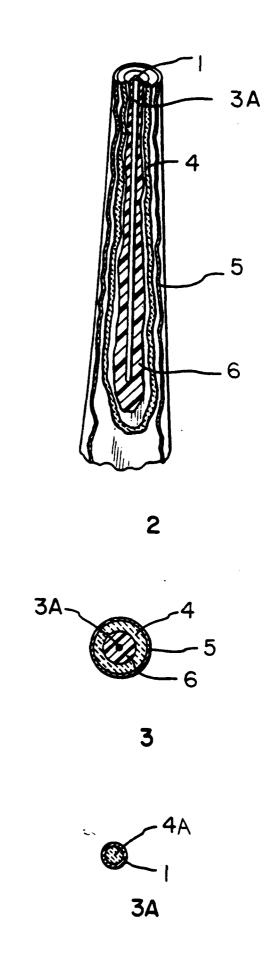
TABLE I. Limiting Current Values as a Function of the Gas Partial Pressure

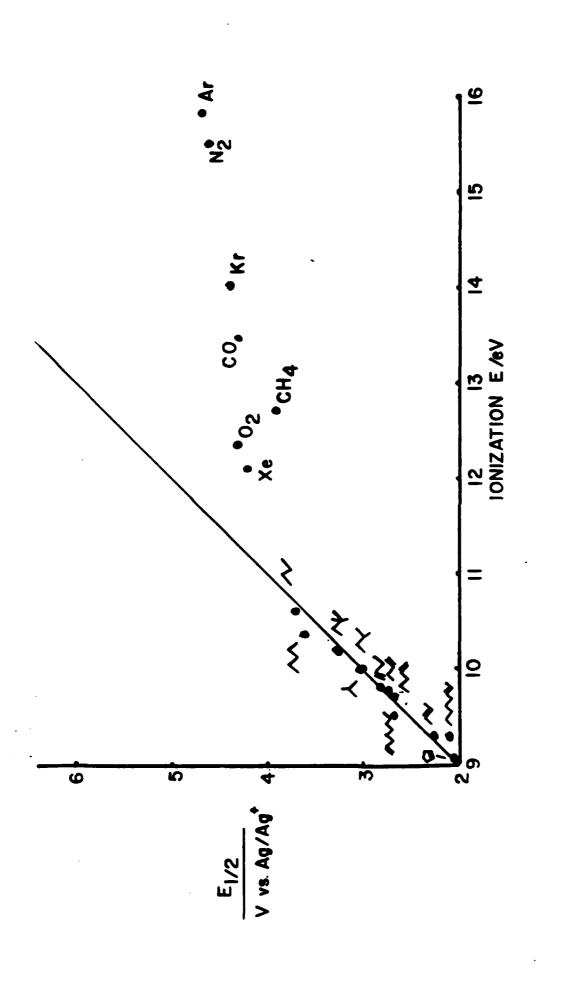
Reactant	Partial Pressure/atm	Limiting Current/nA
Krypton	1.09	1.2
	1.22	1.3
	1.78	2.0
	2.91	3.2
Oxygen	1.10	1.1
	1.90	2.0
	3.12	3.1
Carbon Monoxide	1.23	1.2
	2.64	2.6
	2.98	2.8
Xenon	1.00	1.1
	2.23	2.4
	3.13	3,4

LEGENDS FOR THE FIGURES

- 1. Itramicroelectrode (gold ring) gas phase detector assembly. The sicroelectrode assembly (3A) in this case is constructed of a thin gold film (1) on a glass fiber (4A). The tip cross section (3) consists of the assembly (3A) sealed in a glass tube (4) coated with a thick metal film (5) with epoxy resin (6). (2) details the side view of the tip. A fine copper wire (9) is soldered to the metal film for external contact to the auxiliary/ reference electrode with lead solder (8A), while a similar connection is made to the microelectrode with another copper wire (7) with silver epoxy (8).
- Polarization curve for the oxidation of krypton in acetonitrile solution containing no purposely added supporting electrolyte. Potential sweep rate was $25 \text{ mV}-\text{s}^{-1}$.
- 3. Plot of the vertical ionization potential for several small molecules vs. the measured half wave exidation potential in acetonitrile solution at an extramicroelectrode.







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